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NUCLEUS FORMATION UNDER THE INFLUENCE OF ELECTRICAL CHARGES (DIE KEIMBILDUNG UNTER DEM EINFLUSS ELEKTRISCHER LADUNGEN

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Environmental Protection Agency
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NUCLEUS FORMATION UNDER THE INFLUENCE OF ELECTRICAL CHARGES

(Die Keimbildung unter dem Einfluss elektrischer Ladungen)

by

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Annalen der Physik, Vol.33, 1938 pp 109-131

Preliminary efforts toward a theory of the Wilson chamber were proven unsatisfactory. Especially, agreement with experiments was lacking, and invalid a priori assumptions had been introduced.
A new theory is given that describes the experiments available to-date correctly. However, the value introduced for the dielectric constant cannot yet be purely theoretically justified.
Furthermore, the theory of electrochemical flashover voltage has been developed, that originated from a new phase that needs be separated from the nucleus formation, and was compared with the experiments of T. Erdey-Gruz and H. Wick.

1. Theory of the Wilson Chamber

The droplet formation in supersaturated water vapor, and thereby the whole area of clouds, rainfall and fogformation was, at earlier times, of secondary interest and only a few researchers (1) dealt with the subject. Their qualitative data are not always free of contradictions. It became

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clear, nevertheless, that generally droplet formation occurred on nuclei of some sort that were contained in the vapor. Such nuclei are present as dust either to begin with or they can form there by chemical processes. Of greater interest was the recognition that ions in the air, that had been discovered in connection with the then new, invisible rays, which became increasingly important in physics, could often serve as nuclei for condensation.

C.T.R. Wilson (2) undertook the first systematic investigation of this effect and his work method gave the direction for all later studies. He cooled gas saturated with water vapor suddenly by adiabatic expansion, such as to achieve a supersaturated state which also led to fog formation. The apparatus that he used is essentially still used today in fog-chamber experiments. It consists of an expansion vessel containing air saturated with water vapor. A movable piston connects this vessel with another one, closed off by a stopcock, that can be evacuated. When the stopcock is opened, the rapidly back-sliding piston produces an adiabatic expansion in the observation vessel, that is measured with a mercury manometer. Wilson obtained the degree of expansion, i. e. the volume ratio before and after the expansion, from the pressure measured.

His first data on the graded effectiveness of dust, negative and positive ions, were later partially corrected. Even if all controversy has not subsided to-date, the following seems, nevertheless, to be established: in dust-free air-water vapor mixtures droplet formation occurs with adiabatic expansions whenever the degree of expansion exceeds a value of 1.25. In this case condensation occurs on ions that are always present in the air. At higher ion-content, such as occurs in the presence of X-rays or radioactive substances, this critical expansion limit falls. In a strong electric

field that removes the ions, a degree of expansion of at least 1.28 is necessary to obtain droplet formation. In this case the supersaturated vapor is thus capable of forming droplets spontaneously, i. e. in the absence of condensation nuclei.

It is generally known that Wilson made later the most important discovery that the paths of the various corpuscle rays in his expansion chamber could be rendered visible as fog tracks. Pursuant to this observation, the Wilson chamber has developed, in the last few years, into one of the most indispensable instruments of modern physics, to which most of today's knowledge of atomic nuclei and their elementary particles is owed.

The multi-faceted, impressive results that the use of the Wilson chamber has brought to atomic physics has diverted attention from the essential process of droplet formation. Although a few researchers after Wilson have pursued this field further experimentally, but as for the theory, people generally accepted the solutions given some time ago by J. J. Thomson.

J.J. Thomson (3), in his "theory of the condesation effects of ions", treated the water droplets as conductors with an elementary charge ($e=4.77 \times 10^{-10}$ ESE). Between the radius of such a charged sphere, r, and the vapor pressure, p_r, the following relationship exists:

$$R\,T \ln \frac{p_r}{p_\infty} = \left(\frac{2\sigma}{r} - \frac{e^2}{8\pi r^4} \right) \frac{M}{d}.$$

This function is represented in fig. 1a for T=265° K.(p_∞ is the pressure of saturated vapor above a flat water surface at a temperature T. σ is the surface tension of the water, M the molecular weight and d the density at the same temperature). The curve has a maximum at $\ln p_r/p_\infty = 1.53$, i.e. at $p_r/p_\infty = 4.63$. The right leg of the curve approaches $\ln p_r/p_\infty = 0$

asymptotically at r = ∞, whereas the left branch crosses the axis $\ln p_r/p_\infty = 0$. J.J. Thomson concludes from the progress of the curve that at saturation ($\ln p_r/p_\infty = 0$), or even below saturation ($\ln p_r/p_\infty < 0$) the ion is surrounded by several water molecules, since r is greater than the radius of one molecule. These complexes, however, are unable to grow into droplets. For this, the value $(p_r/p_\infty)_{max.} = 4.63$ must first be reached in J.J. Thomson's opinion. Experimentally, however, it had been found repeatedly that at a critical supersaturation of 4.1 already visible droplets appear.

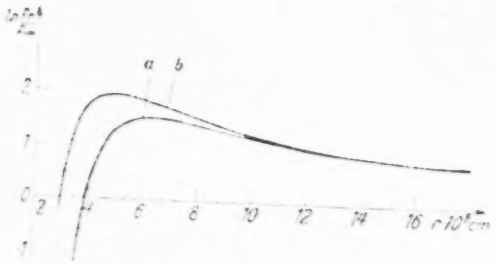

Fig. 1a Vapor pressure of charged water droplets a) conducting, b) not conducting.

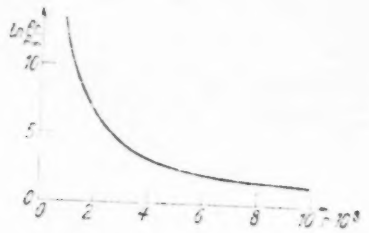

Fig. 1b Vapor pressure of uncharged droplets

Furthermore, Thomson's relation showed no dependency on the number of ions, whereas it had been shown experimentally, that the value for critical supersaturation falls as the number of ions increases. Furthermore, the spontaneous droplet formation in ion-free vapor should be completely impossible. Fig. 1b shows the relation for e=0 (W. Thomson and W. Gibbs). The vapor pressure rises, accordingly, as the radius becomes smaller, such that for $r \to 0$, $p_r/p_\infty \to \infty$. Whereas experimentally spontaneous droplet formation was observed at a degree of expansion of 1.28, i.e. at a supersaturation of 4.9.

From the foregoing it is evident that J.J. Thomson's concept of the

process of droplet formation is not theoretically sound, nor does it agree with present-day experimental results. Droplet formation has to be treated statistically as a process of nucleus formation.

Nucleus formation in ion-free vapor was calculated in different ways using the fluctuation theory of M. Volmer and A. Weber (4), L. Farkas (5), I.N. Stranski and R. Kaischew (6) and later of R. Becker and W. Doering (7), and was found in good agreement with experiment.

T. Glosios (8) already had attempted the calculation for droplet formation on ions. His calculations, however, give only relative values, i.e. it gives the dependency of the critical expansion on the ion content of the vapor. He finis satisfactory agreement with his measurements. According to the "Kinetic treatment of nucleus formation in supersaturated vapor" by R. Becker and W. Doering (7) absolute evaluation is feasible that permits a much more rigorous testing. We intend to expound this theory below and compare it with experiments. Thereby it will be shown - this much we anticipate - that the hitherto accepted concept of the effect of ions, introduced by J.J. Thomson, and taken over by Glosios, has to be changed fundamentally.

The droplets in an ionized vapor-air mixture consist of an ion hydrated by several (10-100) water molecules. If such a droplet is treated as conducting sphere, according to J.J. Thomson, one obtains its free energy by the following consideration: Given is an ion that has the electrical energy $e^2/2r_1$, where e is its charge and r_1 is its radius. We produce such a droplet, containing an ion, in a reversible fashion. Without the charge, formation of a droplet from a large mass of liquid, would require the work σO_r. From this work the electrical energy of the droplet has to be subtracted, which is $(e^2/2r_1 - e^2/2r)$ since the electrical energy falls to $e^2/2r$ as the radius in-

creases from r_1 to r. Hence the work is:

$$F = \sigma O - \left(\frac{e^2}{2r_1} - \frac{e^2}{2r}\right).$$

One obtains the thermodynamic potential in molecular units by differentiation of the free energy with respect to the number of molecules n of the complex and obtains the afore-mentioned equation of Thomson:

$$(1)\quad p_r - p_\infty = kT \ln \frac{p_r}{p_\infty} = \sigma \frac{dO}{dn} - \frac{d\left(\frac{e^2}{2r_1} - \frac{e^2}{2r}\right)}{dn} = \frac{2\sigma}{r}v_0 - \frac{e^2}{8\pi r^4}v_0,$$

where $v_0 = M/d.N$ is the volume that a water molecule occupies in liquid water. The quantities r_a seen on the left part of the curve in fig. 1a that are assigned to the supersaturation p_r/p_∞, are the radii of aggregates, considered spherical, that consist of one ion surrounded by water molecules. No further condensation takes place on these particles. Rather it would be necessary, owing to local density variations in the water vapor, to reach the quantity r_k, namely, the second radius corresponding to p_r/p_∞, that lies on the right part of the curve. It is our task to calculate the frequency of these fluctuations.

Analogous to R. Becker and W. Doering we consider a vessel in which the vapor pressure is kept constant. In the vessel are z_{ion} ions that are in kinetic equilibrium with complexed water molecules. On the average, each ion is complexed with as many water molecules as are required to give an aggregate of radius r_a according to equation (1). As a result of fluctuations, other aggregates, however, are also present. We designate the number of particles that consist of n water molecules with z_n, and with n_K the number of molecules in the droplet nucleus, i.e. in the sphere of radius r_K and with s one that is larger than n_k.

If a particle succeeded to exceed the magnitude of n_K more water can complex with it spontaneously, i.e. it grows to a visible droplet. In order to determine the number of these events we assume that we are able to separate out and count the droplets that have reached the size s. We further assume that the resulting loss of ions and water is compensated by a corresponding supply of more ions and water. In this fashion we construct a stationary state that is amenable to mathematical treatment.

Under these conditions, a constant flow J goes through all z_n that leads droplets with n molecules to those with n+1 molecules. This current has to be calculated.

The probability that one vapor molecule is transformed into a particle with n molecules in time dt is $W_{on}dt$. Conversely, the probability for evaporation from a droplet of n+1 molecules is $W_{on+1}dt$. Then in the steady state:

$$J = z_n \underset{I}{W} O_n' - z_{n+1} \underset{II}{W} O_{n+1}'.$$

The transformation numbers W_{On} and W_{on+1} are dependent of the surface of the droplets and rigorous consideration indicates that the same transitional surface O_n' applies for the forward as well as for the backward reaction. O_n' is the surface of a sphere that surrounds the droplet with n number of molecules and has a radius that is enlarged by the molecular radius.

Therefore:

$$\underset{I}{W} O_n' = \underset{I}{W_n} \quad \text{und} \quad \underset{II}{W} O_{n+1}' = \underset{II}{W_{n+1}},$$

where $\underset{II}{W}_{n+1}$ is still a function of n.

The flow equation becomes:

$$J = z_n \underset{I}{W} O_n' - z_{n+1} \underset{II}{W}_{n+1} \cdot O_n'.$$

setting: $\dfrac{\underset{I}{W}}{\underset{II}{W_n}} = \beta_n$, yields $\dfrac{J\beta_{n+1}}{\underset{I}{W} O_n'} = z_n \beta_{n+1} - z_{n+1}.$

We write these equations for different n from n_a corresponding to radius r_a to n=s one under the other:

$$\frac{J\beta_{n_a+1}}{W\frac{1}{1}O'_{n_a}} = z_{n_a}\cdot\beta_{n_a+1} - z_{n_a+1}\cdot$$

$$\frac{J\beta_{n_a+2}}{W\frac{1}{1}O'_{n_a+1}} = z_{n_a+1}\beta_{n_a+2} - z_{n_a+2}\cdot$$

$$\vdots \qquad\qquad \vdots$$

$$\frac{J\beta_{s-1}}{W\frac{1}{1}O'_{n_K-1}} = z_{n_K-1}\cdot\beta_{n_K} - z_{n_K}\cdot$$

$$\frac{J\beta_s}{W\frac{1}{1}O'_{s-1}} = z_{s-1}\beta_s - z_s\cdot$$

We set $z_s = 0$ and $z_{n\,a} = z_{ion}$. The other z_n cancel by dividing through by the product $\beta_{n_a+1}\cdot\beta_{n_a+2}\cdots\beta_{s-1}$ followed by addition of the equations. Thus we obtain:

$$z_{ion} = \frac{J}{W\frac{1}{1}}\left(\frac{1}{O'_{n_a}} + \frac{1}{\beta_{n_a+1}O'_{n_a+1}} + \frac{1}{\beta_{n_a+1}\beta_{n_a+2}O'_{n_a+2}} + \cdots + \frac{1}{\beta_{n_a+1}\beta_{n_a+2}\cdots\beta_{s-1}O'_{s-1}}\right).$$

If an integral is substituted for the sum and is solved for J, one obtains the fundamental equation:

$$J = z_{ion}\cdot W\frac{1}{1}\int_{n_a}^{n}\frac{1}{O'\prod_{n_a+1}^{n}\beta_i}\,dn.$$

the product $\prod_{n_a+1}^{n}\beta_i = \beta_{n_a+1}\beta_{n_a+2}\cdots\beta_n$ ist: $\prod_{n_a+1}^{n}\beta_i = e^{(n-n_a)\mu_1 - \sum_{n_a+1}^{n}\mu_i}$.

$$\ln\prod_{n_a+1}^{n}\beta_i = \frac{1}{kT}(n-n_a)(\mu_K-\mu_r) - \left[\sum_{n_a+1}^{n}\mu_i - (n-n_a)\mu_r\right].$$

Since: $$\mu_K - \mu_r = \frac{2\sigma}{r_a} v_0 - \frac{e^2}{8\pi r_a^4} v_0 = \frac{2\sigma}{r_K} v_0 - \frac{e^2}{8\pi r_K^4} v_0$$

we get: $$(n-n_a)(\mu_K-\mu_r) = \frac{8\pi}{3}\sigma\left(r_K^3 - r_a^3\right) - \frac{e^2}{6}\left(\frac{r_K^3}{r_K^4} - \frac{1}{r_a}\right),$$

$$\sum_{n_a+1}^{n}\mu_i - (n-n_a)\mu_r = 4\pi\sigma(r^2 - r_a^2) - \frac{e^2}{2}\left(\frac{1}{r_a} - \frac{1}{r}\right).$$

Furthermore:

$$kT \ln \prod_{n_a+1}^{n} \beta_i = \left[\frac{8\pi}{3} \sigma \left(\frac{r^3}{r_K} - r_a^2 \right) - \frac{e^2}{6} \left(\frac{r^3}{r_K^3} - \frac{1}{r_a} \right) \right] - \left[4\pi\sigma (r^2 - r_a^2) - \frac{e^2}{2} \left(\frac{1}{r_a} - \frac{1}{r} \right) \right]$$

$$= -4\pi\sigma r_K^2 \left[\left(\frac{r}{r_K} \right)^2 - \frac{2}{3} \left(\frac{r}{r_K} \right)^3 - \frac{1}{3} \left(\frac{r_a}{r_K} \right)^3 \right] - \frac{e^2}{2} \left[\frac{4}{3r_a} - \frac{1}{3r_K} \left(\frac{r}{r_K} \right)^3 - \left(\frac{r}{r_K} \right)^{-1} \cdot \frac{1}{r_K} \right].$$

We substitute $r/r_K = 1+x$ and expand the r/r_K terms in series. Then, to a first approximation:

$$\left(\frac{r}{r_K} \right)^2 = (1+x)^2 = 1 + 2x + x^2; \quad \left(\frac{r}{r_K} \right)^3 = (1+x)^3 = 1 + 3x + 3x^2;$$

$$\left(\frac{r}{r_K} \right)^{-1} = (1+x)^{-1} = 1 - x + x^2.$$

We obtain:

$$\prod_{n_a+1}^{n} \beta_i = e^{-\frac{1}{kT} \left[x^2 \left(\frac{e^2}{r_K} - 4\pi\sigma r_K^2 \right) \right] - \frac{1}{kT} \left[\frac{4}{3} \pi\sigma (r_K^3 - r_a^3) - \frac{2e^2}{3} \left(\frac{1}{r_a} - \frac{1}{r_K} \right) \right]}.$$

$$\int_{n_a}^{n} \frac{1}{O_K \prod_{n_a+1}^{n} \beta_i} \, dn = \frac{1}{O_K} \int_{n_a}^{n} \left(\frac{n}{n_K} \right)^{-\frac{2}{3}} \cdot e^{-\frac{1}{kT} \left[x^2 \left(\frac{e^2}{r_K} - 4\pi\sigma r_K^2 \right) \right] + \frac{1}{kT} \left[\frac{4}{3} \pi\sigma (r_K^3 - r_a^3) - \frac{2e^2}{3} \left(\frac{1}{r_a} - \frac{1}{r_K} \right) \right]} dn.$$

since: $\frac{r}{r_K} - x + 1 = \left(\frac{n}{n_K} \right)^{1/3}$ we have $dn = 3n_K \left(\frac{n}{n_K} \right)^{2/3} dx$

$$\int_{n_a}^{n} \frac{1}{O_K \prod_{n_a+1}^{n} \beta_i} \, dn = \frac{1}{O_K} \int \left(\frac{n}{n_K} \right)^{-\frac{2}{3}} \cdot e^{-\frac{1}{kT} \left[x^2 \left(\frac{e^2}{r_K} - 4\pi\sigma r_K^2 \right) \right] - \frac{1}{kT} \left[\frac{4}{3} \pi\sigma (r_K^3 - r_a^3) - \frac{2e^2}{3} \left(\frac{1}{r_a} - \frac{1}{r_K} \right) \right]} dx$$

$$= \frac{3n_K}{O_K} e^{-\frac{1}{kT} \left[\frac{4}{3} \pi\sigma (r_K^3 - r_a^3) - \frac{2e^2}{3} \left(\frac{1}{r_a} - \frac{1}{r_K} \right) \right]} \cdot \int e^{-\frac{1}{kT} \left[x^2 \left(\frac{e^2}{r_K} - 4\pi\sigma r_K^2 \right) \right]} dx.$$

The expression under the integral has value significantly different from zero only in the immediate proximity of x=0, therefore we may integrate from $-\infty$ to $+\infty$ without committing an error.

We then obtain:

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{kT} \left[x^2 \left(\frac{e^2}{r_K} - 4\pi\sigma r_K^2 \right) \right]} dx = \sqrt{\frac{\pi kT}{4\pi\sigma r_K^2 - \frac{e^2}{r_K}}}.$$

And:

$$\int_{n_*}^{n} \frac{1}{O_n \prod_{i=1}^{n} \beta_i} dn = \frac{3 n_K}{O_K} e^{-\frac{1}{kT}\left[\frac{4}{3}\pi\sigma(r_K^2 - r_a^2) - \frac{2e^2}{3}\left(\frac{1}{r_a} - \frac{1}{r_K}\right)\right]} \cdot \sqrt{\frac{\pi k T}{4\pi\sigma r_K^2 - \frac{e^2}{r_K}}},$$

$$A_K = \frac{4}{3}\pi\sigma(r_K^2 - r_a^2) - \frac{2e^2}{3}\left(\frac{1}{r_a} - \frac{1}{r_K}\right)$$

we designate as the work required for nucleus formation.

The equation for nucleus formation for charged droplets has the form:

$$J = z_{ion} \cdot W_1 \frac{O_K}{3 n_K} \sqrt{\frac{4\pi\sigma r_K^2 - \frac{e^2}{r_K}}{\pi k T}} \cdot e^{-\frac{1}{kT}\left[\frac{4}{3}\pi\sigma(r_K^2 - r_a^2) - \frac{2e^2}{3}\left(\frac{1}{r_a} - \frac{1}{r_K}\right)\right]}.$$

Comparing with experiments, it is to be noted that the experimental conditions do not strictly correspond to the model that forms the basis for our theoretical treatment. We do not have a stationary flux, but observe a one-time droplet formation. J increases during expansion, reaches a maximal value when expansion is complete, and falls again. The result, namely, the observed number of droplets, represents a time integral that we need not, however, to calculate. Because with increasing supersaturation, J increases so rapidly that in actual practice only the state of maximal expansion need be considered. We can, therefore, set $\int J\,dt = J\,\Delta t$ where Δt signifies the duration of the maximal supersaturation state, which is about one second under the experimental conditions, according to measurements of H. Flood (9). If we choose, for observation, the supersaturation at which the first droplets just form, one can assume that droplet formation proceeds practically without loss of ions and water vapor and that, therefore, the theoretical conditions are satisfied.

The experimental results for the critical supersaturation of water vapor in dust-free air are summarized in table I.

Table I (10)

a) Name	b) Temperatur °K	c) Exp.grad $\left(\frac{V_1}{V_2}\right)_{kr}$	d) Übersättigung $\left(\frac{p_r}{p_w}\right)_{kr}$
Aitken	261	1,333	6,8
Wilson	267,9	1,252	4,1
Donnan	264,7	1,29	5,0
Barus	259	1,363	7,3
Laby	267,6	1,256	4,2
Besson	268,1	1,25	4,1
Strieder	267,8	1,253	4,1
Andrén	267,8	1,253	4,1
Anderson u. Froemke	—	1,200	3,0
Flood[9]	265	1,252	4,1

a) name; b) temperature; c) degree of expansion; d) supersaturation.

It can be seen that the most frequent value for the critical supersaturation is that already found by Wilson, namely $(p_r/p_w)_{kr} = 4.1$. The values obtained by Aitken, Barus and Donnan are so completely outside the range that we need not consider them. The value obtained by Anderson and Froemke also diverges widely. These researchers applied significantly more rapid expansion, on the assumption that the earlier expansions did not occur adiabatically. As Flood (9) has shown by direct measurement, these objections are unfounded; on the contrary, too rapid expansion produces convective currents that cause disturbances. We may, therefore, consider $(p_r/p_w)_{kr} = 4.1$ correct and use this value in a comparison with the theoretical derivation.

In practical evaluation the factor in front of the e-term has to be determined first. Essentially, it contains, in addition to the number of ions, the quantity W_I. Now $W_I = 1/4\ n\bar{c}$, where n is the number of molecules of water vapor per cubic centimeter and $\bar{c}$ their mean velocity. The natural ion content of air is given with $z_{ion} = 10^3$. Since $\Delta t = 1$, we obtain:

$$\ln z_{ion} \cdot W \frac{O_K}{3 n_K} \cdot \sqrt{\frac{4 n a r_K^2 - \frac{e^2}{r_K}}{a k T}} = 22{,}9 .$$

Therefore:

$$\ln J = 22{,}9 - 0{,}907 \cdot 10^{16}(r_K^2 - r_a^2) - 430 \cdot 10^{-8}\left(\frac{1}{r_a} - \frac{1}{r_K}\right).$$

From this, and J.J. Thomson's equation

$$\ln J = f(\ln pr/p_{\infty})$$

was determined and plotted as in fig. 2a. For ln J = 0 one obtains $\ln(p_r/p_\infty)_{kr}$ = 1.19, or $(p_r/p_\infty)_{kr}$ = 3.3, which is much smaller than the experimentally determined value of 4.1. For p_r/p_∞ = 4.1 one obtains ln J = 25, i.e. $J = 10^{10}$, or a 10^{10} times greater droplet formation than had been found experimentally. The number of droplets, of course, has an upper limit which is set by the number of ions of 10^3, but the error of the theoretical calculation remains untouched by the experimental impossibility.

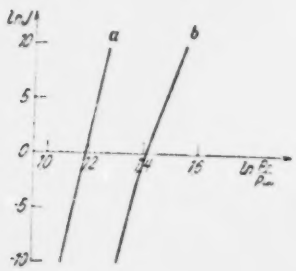

Fig. 2a. ln J as a function of ln p_r/p_∞ for a) conducting, b) non-conducting water droplets

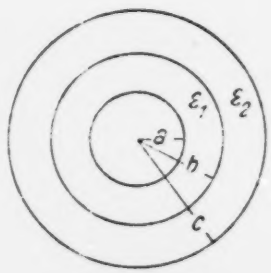

Fig. 3. Model of a shperical condenser.

The maximal error in our evaluation, however, can be of the order of 10^2 due to deviations from the average number of ions 10^3 or from a condensation coefficient $\alpha < 1$.

The actually existing, enormous discrepancy cannot be understood in this way, but must be looked for in a more profound cause concerning the basic

assumptions.

Under more careful scrutiny the assumption made up to now, to consider the water droplets conducting spheres, appears completely unjustified. Because droplets having such radii as we have been considering and that correspond to a number of molecules of 10-100, cannot possess conductivity, since for the degree of dissociation of water ($3x10^{-10}$) only in a drop of $1/3x10^{10}$ molecules would, on the average, one H^+ and one OH^- be present. Our small droplets should doubtless be treated as dielectrics. We shall, therefore, modify the theoretical treatment accordingly.

We calculate the electrical contribution to the thermodynamic potential of a dielectric sphere with a central charge. For the solution of this problem we use the model of a spherical condenser (fig. 3).

The space between two surfaces within the sphere shall be filled by two media of dielectric constants ε_1 and ε_2, separated by a third spherical plane. The radii of the three spherical planes be a, b, c, from the center to the surface. Since the field strength is given by $\mathfrak{E}_r = \frac{1}{\varepsilon_1}\frac{e}{r^2}$ and $\mathfrak{E}_r = \frac{1}{\varepsilon_2}\frac{e}{r^2}$ the potential difference between spheres a and c becomes:

$$V = \int_a^c \mathfrak{E}_r\, dr = \frac{e}{\varepsilon_1}\left(\frac{1}{a} - \frac{1}{b}\right) + \frac{e}{\varepsilon_2}\left(\frac{1}{b} - \frac{1}{c}\right) = \frac{e}{b}\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right) + \frac{e}{\varepsilon_1 a} - \frac{e}{\varepsilon_2 c}.$$

The capacity is given by $C = e/V$. Therefore:

$$\frac{1}{C} = \frac{1}{b}\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right) + \frac{1}{\varepsilon_1 a} - \frac{1}{\varepsilon_2 c}.$$

As $c \longrightarrow \infty$, $\varepsilon_2 = 1$ so that this model corresponds to our complex. Then:

$$\frac{1}{C} = \frac{1}{b}\left(1 - \frac{1}{\varepsilon_1}\right) + \frac{1}{\varepsilon_1 a}.$$

The electric energy of this complex of radius r is:

$$E_{el} = \frac{1}{2}\frac{e^2}{C} = \frac{1}{2}\frac{e^2}{r}\left(1 - \frac{1}{\varepsilon}\right) + \text{konst.}$$

When differentiated with respect to the number of molecules, the wanted electrical term of the thermodynamic potential is:

$$\frac{dE_{el}}{dn} = \frac{1}{2} e^2 \left(1 - \frac{1}{\varepsilon}\right) \frac{d\left(\frac{1}{r}\right)}{dn} = - \frac{e^2 \left(1 - \frac{1}{\varepsilon}\right) r_0}{8\pi r^4}$$

The expression for a dielectric complex differs, therefore, by a factor (1 - 1/s) from that for a conducting sphere.

If we substitute for ε the dielectric constant $\varepsilon = 80$, the result is practically unchanged. It is, however, doubtless incorrect to assume the dielectric constant 80 of water for these droplets, whose molecules are subjected to the strong field of the central ion. The major component of the value of 80 during the measurement of the dielectric constant is, as is well-known, the orientation of the dipole. If this orientation is totally or partially obviated, as a result of an already existing orientation in a strong field, the dielectric constant must necessarily fall considerably.

Measurements of dielectric constants of water bound to dipoles (metal-oxides or oxyhydrates) give an indication of the order of magnitude at which the in this case relevant value of ε is to be expected. From pertinent data of Glemser (11) it can be seen that values between 1.1 and 6, depending on the water content and the strength of the binding, are to be found.

Independently of the foregoing, the following consideration of the physical characteristics of our charged droplets can be made, that leads directly to the view that the vapor pressure of the small droplets is not decreased by the central charge to an extent as would be the case for charged spheres or spheres of a very high dielectric constant.

The effect of the central charge, in a centrifugal direction, on the dipoles and their respective orientation, is to lessen the binding. The heat

of condensation of the water results from two causes: first from London's polarization forces and second from dipole formation. The latter claims a large share. In order to estimate this, we compare with van Arkel and de Boer (12) the heat of vaporization on the one hand, and on the other the polarizability and the dipole moment of the related compounds H_2O and H_2S.

Table II

H_2O	H_2S	
3.76	9.57	Molecular refraction (proportional to polarizability
1.85	0.93	permanent dipole moment
+ 100	− 60	boiling temperature °C.

If only the contribution due to the polarizability were decisive, the heat of vaporization and also, according to Trouton's rule, the boiling point, of H_2S should be higher than that of H_2O. In actual fact, however, the boiling point for H_2S lies considerably lower than for H_2O. Consequently, the permanent dipole moment and not the polarizability must have the main effect on the heat of vaporization. Since for our droplets the permanent dipole moment is largely canceled by the ion, this should lead to a large decrease in the heat of vaporization. Therefore, the vapor pressure of the droplet cannot be reduced by the charge to the same extent as would be the case for a droplet of a conducting or of a dipole-free liquid.

Since we cannot carry out calculations of a possible ε-value based on a model, which might be possible based on quantum mechanics, we proceed by a method of successive approximations to find a ε-value compatible with the experiment. In this way one finds $\varepsilon = 1.85$.

J.J. Thomson's equation then becomes:

$$\ln \frac{p_r}{p_\infty} = \frac{12.6}{r} \cdot 10^{-7} - \frac{345}{r^3} \cdot 10^{-21}$$

and is plotted in fig. 1a (b). The equation for ln J is:

$$\ln J = 22{,}9 - \left[0{,}907 \cdot 10^{16}\,(r_K^2 - r_0^2) - 198 \cdot 10^{-8}\left(\frac{1}{r_a} - \frac{1}{r_K}\right)\right].$$

The dependency of ln J on ln p_r/p_∞ can be seen from fig. 2b.

For natural as well as induced ionization of different strengths, there exists, in every case, a corresponding value for the critical supersaturation:

Table III.

n_{ion}	$\left(\frac{p_r}{p_\infty}\right)_{kr}$
10^3	4,1
10^4	3,99
10^5	3,9

Data in the literature for the experimentally determined values of $(p_r/p_\infty)_{kr.}$ obtained with artificial ionization diverge widely (table IV).

Table IV (10)

a) Name	b) Temp. °K	c) Exp.grad $\left(\frac{V_1}{V_2}\right)_{kr}$	d) Übersätt. $\left(\frac{p_r}{p_\infty}\right)_{kr}$	e) Ionisiert durch
Wilson	290,1	1,260	5,0	stark. ultraviol. Licht f)
Wilson	288,2	1,219	4,0	Uranoxyd g)
Wilson	288,3	1,247	4,9	Röntgenstrahlen h)
Pickeam	290,8	1,265	5,1	Ra Präparat i)
Barus	291,8	1,325	5,9	Radium k)
Barus	292,3	1,320	5,8	Röntgenstrahlen l)
Mme Curie. . .	293,1	1,060	1,0	Radon m)
Luby	289,3	1,250	3,5	Röntgenstrahlen n)
Besson	289,1	1,245	3,5	" o)
Besson	289,1	1,245	3,5	Radium " p)
Leibfried . . .	292,5	1,095	1,03	Röntgenstrahlen q)
Conrad	290,1	1,060	1,0	" r)
Strueder	293,1	1,060	1,0	" s)
Andrée	270,4	1,225	3,0	Ra-Präparat t)
Powell	268,6	1,244	4,0	Gammastrahlen u)

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a) name; b) temperature; c) degree of expansion; d) supersaturation; e) ionized by; f) strong ultra-violet light; g) uranium oxide; h) X-rays;

key to table IV continued:

i) Ra-preparation; j) radium; l) radon; m) gamma-rays.

Neglecting those experiments that did not give any supersaturation - that were apparently spurious for reasons that could later no longer be determined - and those of Pribram and Barus because of their conspicuous, certainly too high values, 7 different data for the critical supersaturation remain that lie between 3.6 and 4.0. In addition there are the survey measurements of T. Glosios who has also determined the approximate ion content.

At this time we can only conclude that the critical supersaturation falls insignificantly with increased ion content.

Because of the importance of the Wilson chamber for observing ray-tracks, the values of the term $(p_r/p_\infty)_{kr}$ is of interest, where a droplet is formed on every ion with a probability of 1. This can be taken from the curve $p_r/p_\infty = 4.6$ and thereby lies below 4.0, the value of the term $(p_r/p_\infty)_{kr}$ for ion-free vapor at the same temperature. This is of decisive importance for the use of the Wilson chamber.

The supersaturation for several other vapors was determined using our formula in analogous fashion. We use again the experimental results of H. Flood (table 5)

Table V (9)

Stoff	Temperatur °K	Exponent $\left(\frac{V_1}{V_2}\right)_{kr}$	Übersättigung $\left(\frac{p_r}{p_\infty}\right)_{kr}$
Wasser	283	1,27	4,1
Äthylalkohol	270	1,11	2,1
Nitromethan	255	1,42	5,25
Äthylazetat	247	1,53	7,0
Äthylazetat	245	1,62	9,2
Essigsäure	245	1,67	11,0
Cyclohexan	228	2,35	17,0
n-Heptan	231	1,99	18,0

Key to table V: a) substance; b) temperature; c) degree of expansion; d) supersaturation; e) water; f) ethanol; g) nitromethane; h) ethyl acetate; i) ethyl acetate; j) acetic acid; k) cyclohexane; l) n-heptane.

From these data ethanol, nitromethane and ethyl acetate were chosen for the calculation of the supersaturation. A comparison of the measured results on acetic acid, cyclohexane and n-heptane is meaningless, since the critical degree of expansion of their vapors lies considerably above 1.5. But according to the observations of H. Flood, adiabatic expansion can only take place up to a value of $(V_1/V_2)_{kr}$=1.5. Even ethyl acetate that had been included, lies, strictly speaking, above that limit with a value of $(V_1/V_2)_{kr}$ = 1.575.

The critical supersaturation for ethanol (fig. 4a, 4b) gives $(p_r/p_\infty)_{kr}$ = 2.07 in good agreement with the value found by H. Flood (2.1). The dielectric term is set $(1-1/\varepsilon) = 1$. That means, that in order for the term $(1-1/\varepsilon) = 1$, the dielectric constant ε must assume a value of 28.4.

For nitromethane $(P_r/p_\infty)_{kr}$ = 4.33 (fig. 5a, 6a), when $(1-1/\varepsilon)$ is set equal to 1. The experimentally obtained value $(p_r/p_\infty)_{kr}$= 5.25 (fig. 5b, 6b) when $(1-1/\varepsilon)$ = 0.53, or ε = 1.38.

For ethyl acetate a value of $(p_r/p_\infty)_{kr}$ = 5.28 (fig. 7a, 8a) corresponds to $(1-1/\varepsilon) = 1$, whereas for a value of $(1-1/\varepsilon)$ = 0.38, or ε = 1.27, a critical supersaturation of $(p_r/p_\infty)_{kr}$ = 7.6 (fig. 7b, 8b) is obtained. For nitromethane and ethyl acetate, just as for water, only a part of the dielectric constant is effective.

In view of the theoretical insight gained, experiments with really conducting droplets, such as can be produced in the Wilson chamber in the presence of HCl, would be of interest. In this case the critical degree of

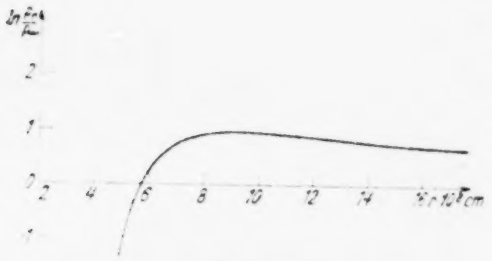

Fig. 4a. Vapor pressure of charged ethanol droplets.

Fig. 4b. ln J as a function of ln p_r/p_∞ for ethanol droplets.

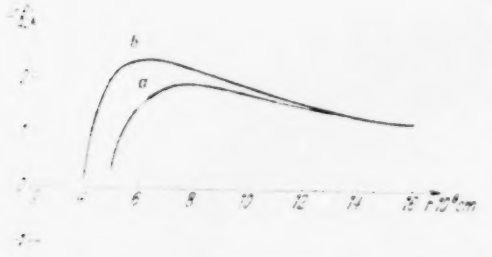

Fig. 5. Vapor pressure of charged nitromethane droplets.

Fig. 6. ln J as a function of ln p_r/p_∞ for nitromethane droplets.

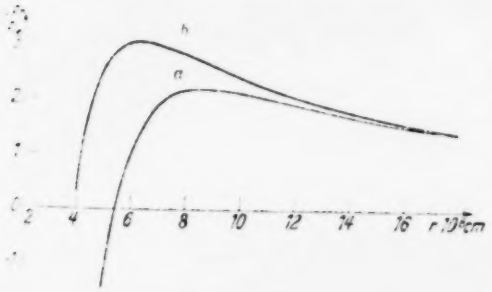

Fig. 7. Vapor pressure of charged ethyl acetate droplets.

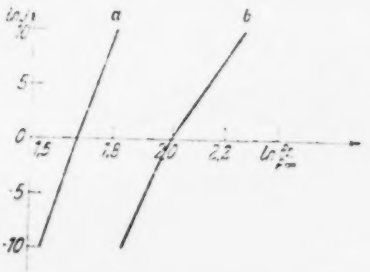

Fig. 8. ln J as a function of ln p_r/p_∞ for ethyl acetate droplets.

expansion would have to lie considerably lower and the difference of the value for ion-free vapor would have to be greater.

Experiments with vapors without dipole molecules would also be required for a further clarification.

The difference in effectiveness of positive and negative ions claimed

by C.T.R. Wilson, but to-date not proven, would deserve checking. A purely theoretical investigation is not possible without an accurate understanding of the structure of the smallest aggregates.

2. Electrolytic Nucleus Formation

In connection with the work on droplet formation on ions, the electrolytic deposition of droplets on electrodes was also theoretically treated.

This type of nucleus formation is distinguished from the former by the fact, that molecules or atoms do not form droplets by coalescing in free space, but that ions are deposited on the cathode of an electrolytic vessel where they coalesce to form more or less spherical aggregates.

During nucleus formation on ions in water vapor saturated air the droplets form as spherical condensers, whose secondary coating lies in infinity. In electrolytic metal deposition we deal with condensers of finite plate distance, formed according to the double layer of Helmholtz.

It is convenient to use, in their description, the electrochemical potential defined by E. Lange and K. Nagel (13): $\eta = \mu + He$. where e is the charge on the ion and H is the electric potential inside the phase. As an example we choose the deposition of mercury from a solution of mercuric ions on a carbon electrode that cannot be completely wetted by mercury. Fig. 9 shows the experimental design.

At the bottom of the decomposition cell an amount of mercury II' forms the anode that exposes a large surface to the electrolyte I. A cathode made from material III dips into it, on which the new phase II, namely mercury, shall be deposited. A battery serves as the source of current that is connected to the cell in form of a potentiometer.

Phases II' and I are in a state of equilibrium at the minimal currents used, i.e. the electrochemical potentials of the mercury II' and the electrolyte I are equal: $\eta_{II'} = \eta_I$. If the new phase II existed in contact with the electrode III and exposing a flat surface to the electrolyte, its electrochemical potential would be: $\eta_{II} = \mu_{II} + H_{II}c$. and since: $\mu_{II} = \mu_{II'}$, we get:

$$\eta_{II} = \eta_{II'} + (H_{II} - H_{II'})c = \eta_{II'} - Ec = \eta_I - Ec.$$

In case that in forming the new phase II, the mercury is deposited in the form of a lense, whose wetting angle, at the applied voltage, is (E) φ and whose radius of curvature is r, the modified Thomson-Gibbs equation becomes:

$$(\eta_r - \eta_\infty)_{II} = \frac{2\sigma_{I\,II}\,\omega'\omega}{r}$$

where the index I/II corresponds to the phase limit I/II. If q is the capacity of the double layer per cm^2, then:

$$\sigma_{I\,II(E)} = \sigma_{I\,II\,max} - \frac{1}{2}(E - E_{max})^2 q.$$

We set $q = \frac{1}{4\pi\delta}$, where δ is the distance between the plates divided by the dielectric constant. According to the measurements of M. Gouy (14) δ has a value between 0.2 - 0.5 x 10^{-8} cm, which is small compared to molecular dimensions. $\sigma_{I/II\,max}$ is the maximal voltage at the interphase that occurs at a charge 0 of the condenser and the corresponding electromotive force E_{max}.

Therefore: $$\sigma_{I\,II(E)} = \sigma_{I\,II\,max} - \frac{(E - E_{max})^2}{8\pi\delta}.$$

In order to determine the frequency of nucleus formation we imagine a large number of lenses of sizes below that necessary for nucleus formation, distributed over the surface of the cathode III, that can take up or give

up ions. If one of our complexes exceeds the threshold for nucleus formation it grows into a lense that we remove, or let drip off, when the number of atoms s ($s \gg n_K$) reaches this value.

The set-up is here completely analogous to that for droplet formation in vapor. From the formulae for the elementary process:

$$J\,dt = \underset{\text{I}}{W} Z_n O_n\,dt - \underset{\text{II}}{W}_{n+1} Z_{n+1} O'_n\,dt$$

we get: $$\frac{J}{W}\left(\frac{1}{O_1} + \frac{1}{\beta_1 O'_1} + \frac{1}{\beta_1\beta_2 O'_2} + \cdots + \frac{1}{\beta_1\beta_2\cdots\beta_n O'_n} + \frac{1}{\beta_1\beta_2\cdots\beta_{n-1} O_{n-1}}\right) = z_0 .$$

All β - and O'-values from 1 to s must appear in the sum, since the mercury lense forms by stepwise deposition of single ions and we do not proceed, as with a vapor, from an aggregate that consists already of several molecules (n_0). Furthermore z_0 is the number of places on the surface of the cathode in lieu of z_{Ion}, the number of ions. First we evaluate the product:

$$\prod_1^n \beta_i = \beta_1\beta_2\cdots\beta_n = e^{\eta_1 - \sum \eta_{Ki}} .$$

We expand the sum in the exponent as we did previously, whereby we abbreviate: $\eta_{III} = \eta_{II}$ and write:

$$n\,\eta_I - \sum_1^n \eta_i = n(\eta_I - \eta_{II}) - \left(\sum_1^n \eta_i - n\,\eta_{II}\right).$$

We can substitute η_{IIrK} for η_{I} since the nucleus is in equilibrium with the electrolyte.

Therefore, we get:

$$n(\eta_I - \eta_{II}) = n\frac{2\sigma_{II}\,r^2}{r_K} = \frac{2\sigma r^2(2 - 2\cos\varphi\sin^2\varphi\cos\varphi)\,\sigma_{III}}{3r_K}$$

since nv_0 equals the volume of the lense with a radius of curvature r,

namely $n r_0 = \frac{1}{3}\pi r^3(2 - 2\cos\varphi - \sin^2\varphi\cos\varphi)$. The second term in the sum is the work required for reversible formation of the lense of a larger quantity of mercury, that is in conducting connection with the cathode (III). This is only a surface activity A_{σ}, whereby:

$$A_o = [\sigma_{I\,II}\cdot O_{I\,II} + (\sigma_{II\,III} - \sigma_{I\,III})O_{II\,III}]_E$$
$$= \sigma_{I\,II(E)}\cdot O_{I\,II} - \sigma_{I\,II(E)}\cdot\cos\varphi\, O_{II\,III},$$

since it follows from the equilibrium of forces at the edge of the lense:

$$[\sigma_{I\,III} = \sigma_{II\,III} + \sigma_{I\,II}\cos\varphi]_E.$$

When ϱ is the radius of the circular surface of contact $O_{II/III}$, then:

$$O_{II\,III} = \pi\varrho^2 = \pi r^2\sin^2\varphi.$$

Furthermore:

$$O_{I\,II} = 2\pi r h = 2\pi r^2(1 - \cos\varphi) \quad (h = \text{height of the lense})$$

Then:

$$A_o = \sigma_{I\,II(E)}\cdot\pi r^2(2 - 2\cos\varphi - \sin^2\varphi\cos\varphi).$$

The total sum then has a value of:

$$n A_{II} - \sum_1^n A_o = -\sigma_{I\,II(E)}\cdot\pi r_K^2(2 - 2\cos\varphi - \sin^2\varphi\cos\varphi)$$
$$\cdot\left[\left(\frac{r}{r_K}\right)^2 - \frac{2}{3}\left(\frac{r}{r_K}\right)^3\right] = -A_K\left[3\left(\frac{r}{r_K}\right)^2 - 2\left(\frac{r}{r_K}\right)^3\right].$$

$A_K = \frac{1}{3}\sigma_{I\,II,E}\cdot\pi r_K^2(2 - 2\cos\varphi - \sin^2\varphi\cos\varphi)$ designates the work required for nucleus formation.

Analogous to the calculation for droplet formation on ions in a air-vapor mixture we obtain from:

$$J = z_0 W_1 \int_1^{\infty} \frac{1}{O_n \prod_1^n \beta_n}\, dn$$

the result: $J\,dt = W_1 \frac{z_0 O_K}{n_K}\cdot\sqrt{\frac{A_K}{3\pi k T}}\cdot e^{-\frac{A_K}{kT}}\cdot dt.$

since $r_K = \frac{2\sigma_{I\,II,E}\cdot v_0}{n_K}\cdot\sqrt{\frac{A_K}{3\pi k T}}\, e^{-\frac{A_K}{kT}}.$

becomes:

$$A_K = \frac{4\pi}{3} \cdot \left[\sigma_{I/II\,max} - \frac{(E - E_{max})^2}{8\pi\delta}\right]^2 \cdot r_0^2 (2 - 3\cos\varphi - \sin^2\varphi\cos\varphi)$$

Furthermore, within the area considered for practical purposes, we approximate: $\frac{z_0 O_K}{a_K} \cdot \sqrt{\frac{A_K}{3\pi kT}} \approx z_0 O_0 \approx O_{III}$.

i. e. is about equal to the surface area of the cathode. $W_{I}^{O}{}_{III}$ is the number of ions that strike this surface, i.e. $J\,\Delta t \approx W_{I} O_{III} e^{-\frac{A_K}{kT}} \Delta t$.

The measurements of M. Gouy on the electro-capilarity of mercury (fig. 10) permit a comparison with the experiment. It is apparent that generally the dependency of the voltage of the separating surface Hg/electrolyte on the potential cannot be represented by the formula $\sigma_{I/II\,max} - \frac{(E - E_{max})^2}{8\pi\delta}$ over the entire range. Within the range pertinent for nucleus formation a satisfactory agreement with the measurements of Gouy can be achieved by a suitable choice of the constants $\sigma_{I/II\,max}$ and δ.

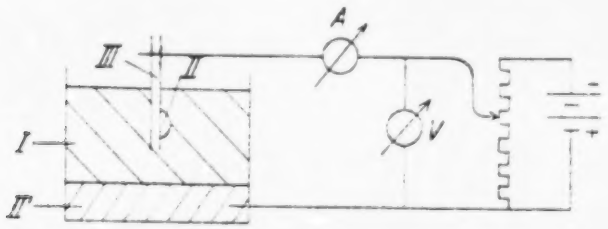

Fig. 9. Electrolytic cell with mercury anode (II'), a solution of a mercuric salt (I), carbon electrode (III), deposited mercury droplets (II).

In practice one proceeds by calculating ln J Δ t for several voltages E, whereby the respective values for σ can be taken directly from the curves of Gouy (fig. 10). It is to be remembered that our E-values are in

terms of the electrode I/II', whereas there they are based on the normal kalomel electrode.One has to measure,therefore, in every case, the combination I/II' used against the kalomel electrode.

Observations on nucleus formation were done by T. Erdey-Gruz and H. Wick (15). A saturated solution of mercuric acetate in n-acetic acid was used as electrolyte. It is 0.0009 normal. The use of such dilute solution is profitable because after nuleation has taken place, the solution in the immediate proximity of the mercury lense is so depleted of mercuric ions, that further deposition does not occur in this place, so that this nucleus is, for practical purposes,removedfrom the solution. Also, the state of polarization of the cathode remains unchanged local concentration dependent polarization and one can pursue one's observations.

Gouy has performed measurements of surface tension in acetic acid that are useful. Unfortunately, he gives only relative potential-values, setting arbitrarily $\sigma_{(E)}$ = 384 dyn/cm on the descending slope of the electro-capillary curve E=2, for all solutions. Based on data available for acids of similar concentrations (about n/100), we are able to assign to the value E=2 a value of E_{cal} = -1.18 volt, on the normal kalomel electrode. The error in this assignment is maximally of the order of 0.01 to 0.02 volt, since the cathodic slopes of all curves nearly coincide also in absolute terms. The resting potential of the anode (I/II') used by Erdey-Gruz and Wick was determined as +0.384 volt on the normal kalomel electrode. The applicable potentials against the anode are marked, in fig. 10, as well as the $\sigma(E)$ -values that were used in the calculations for the ln J-curve.

The limiting surface tension in dyn/cm over the useful range is given by the formula:

$$\sigma_{(E)} = 425 - \frac{(E - E_{max})^2}{8\pi \cdot 0{,}39 \cdot 10^{-8}} \quad (E - E_{max} \text{ in ESE})$$

(425 dyn/cm is not the true value of σ_{max}, but rather a constant which, over the pertinent range, gives the correct value of $\sigma_{(E)}$).

The determination of the wetting angle is generally difficult because a high degree of accuracy is required. Only as φ approaches 180° is an approximate determination sufficient. For the carbon electrodes used by Erdey-Gruz and Wick it was later established that under the experimental conditions mercury droplets were deposited with a contact area whose diameter amounted to about 1/3 of the diameter of the sphere.

From that one calculates $\varphi = 146°42'$ and:

$$2 - 2\cos\varphi - \sin^2\varphi\cos\varphi = 2 + 2 \cdot 0{,}944 + 0{,}1 = 3{,}988 \approx 4$$

as large as for a complete sphere, where $\varphi = 180°$. Consequently, the accurate measurement of such obtuse wetting angles is insignificant for the calculation. The ionization of mercury occurs without marked polarization, i.e. the activation energy is only kT. In this case W_I is of the same order of magnitude as the gaskinetic number of collisions of the ions per cm^2/sec.. Since the acetic acid is in large excess the double layer is formed practically only from its ions and an increase in the number of collisions corresponding to the zeta-potential can be neglected. Thus one obtains for the prevailing conditions:

$$W_I \sim \frac{1}{4} n_{Hg^+} + \bar{c}_{Hg} \sim 10^{21}.$$

The surface area of the cathode was $O_{III} = 1/10$ cm^2, the time interval between nucleus formations 10 sec. Therefore, the equation for $\ln J\,\Delta t$ is:

$$\ln J\Delta t = 48{,}3 - \frac{16\pi\,\sigma^3_{(E)} v_0^2}{3(Ee)^2 kT} = 48{,}3 - 0{,}974 \cdot 10^{-7} \cdot \frac{\sigma^3_{(E)}}{E^2_{Volt}}.$$

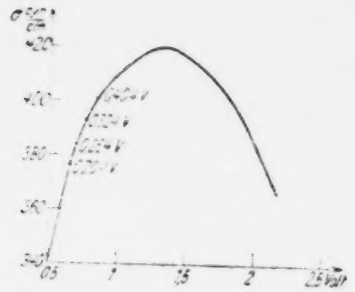

Fig. 10. Electro-capilarity of mercury in acetic acid.

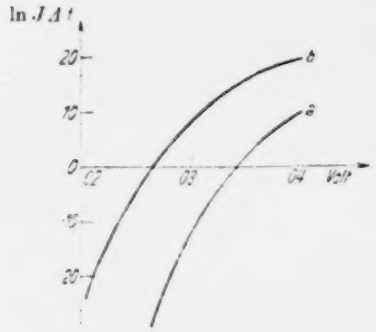

Fig. 11. ln J Δt as a function of the voltage

Fig. 11 shows the dependency of ln J Δt on E. The metastable limit lies at 0.34 Volt.

Erdey-Gruz and Wick found that the first nucleus formation on carbon-electrodes with essentially smooth surfaces occur at E = 0.2 volt and could be studied up to 0.27 volt. It can be observed by the sudden fall in voltage and a rise in current. As can be seen, the theoretical value of 0.34 volt is not reached. The explanation is evident. The microscopically observed wetting angle is not the decisive one. It suffices that sections of about ten-fold the linear atomic size have a better wettability due to special arrangement of the carbon atoms in order to facilitate nucleation on these "active sites". If, for instance, in such places $\gamma = 90^{\circ}$, then $A'_K = 1/2\ A_K$. And if these places amounted to the 10^4th part of the surface area, then:

$$\ln J\Delta t = 39 - \frac{3\pi\sigma^3 E^{*2}}{3(Ee)^2 kT}$$

This curve is also shown in fig. 11(b). The metastable limit would then be at 0.272 volt.

Furthermore, even the most carefully produced surfaces are not perfectly smooth, despite high gloss. Every groove, however, decreases the work required for nucleation.

On unpolished surfaces nucleus formation could be observed already at 0.15 volt. Traces of metal lower the threshold even more, e.g. it was sufficient to touch the carbon rods with bone forceps, that had been previously used in weighing, to make the excess voltage disappear.

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